THE NATURE AND REACTIONS OF HALOGEN ADDENDS OF THE SILVER FLUOROCARBON CARBOXYLATES

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By

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TABLE OF CONTENTS

		Page
LIST OF TABLES		iv
LIST OF ILLUSTRATIONS		vi
I.	INTRODUCTION	1
II.	PREPARATION, ISOLATION, AND IDENTIFICATION OF THE COMPLEXES	13
	Determination of Extent of Reaction	
	Analysis of Reaction Mixtures	
	Analysis of the Complexes in Solution	
	Isolation of the Solid Complexes	
III.	USES OF THE COMPLEXES IN THE SYNTHESIS OF FLUOROCARBON DERIVATIVES	47
	General Discussion	
	Substitution of Pyridine for X in the Complex-Forming Reaction	
	An Improved Method for the Synthesis of Fluorocarbon Mono-Iodides	
	Reactions of (S) and the Complex with Phosphorus	
IV.	RELATED SYNTHETIC PROCEDURES	63
	Preparation of Fluorocarbon Nitriles from (S) and Cyanogen	
	Synthesis of Fluorocarbon Mono-Iodides from Fluorocarbon Carboxylic Acid Anhydrides	
V.	DISCUSSION OF RESULTS	67
VI.	BIBLIOGRAPHY	75
VII.	VITA	78

LIST OF TABLES

Table		Page
1.	Source and Purity of Materials Used in the Investigations Herein Reported	23
2.	Preliminary Experiments Determining the Stoichiometry of the Reaction of Silver Acetforate with Iodine or Bromine in Various Solvents	24
3.	The Stoichiometry of the Reaction of Silver Salts of Fluorocarbon Carboxylic Acids with Iodine or Bromine in Fluorocarbon Solvents	26
4.	Measurement of Excess Iodine Present in Solutions of Reaction Mixtures by the Color Comparison Method	27
5.	Preparation and Analysis of Reaction Mixtures of Silver Salts of Fluorocarbon Carboxylic Acids and Iodine or Bromine	
	A. Preparation	35
	B. Analysis	36
6.	Analysis of the Complexes in Solution in Fluorocarbon Solvents	
	A. Relationship Between Acid Number, Oxidizing Power, and Recoverable Silver	40
	B. Comparison of the Stabilities of the Complexes in Solution	41
7.	Preparation, Isolation, and Analysis of the Solid Complexes	46
8.	Preparation and Analysis of the Pyridine Addends of the Silver Fluorocarbon Carboxylates	52
9.	Improved Synthesis for Fluorocarbon Iodides	
	A. Procedure 1	59
	B. Procedure 2	59

LIST OF TABLES--Continued

Table		Page
10.	Preparation of Fluorocarbon Nitriles by the Decarboxylation of Silver Salts of Fluorocarbon Carboxylic Acids in the Presence of Cyanogen	
	A. Experimental Data	66
	B. Analytical Data	66
11.	Preparation of Fluorocarbon Iodides from Fluorocarbon Carboxylic Acid Anhydrides	70

LIST OF ILLUSTRATIONS

Figure		Page
1.	.....	30
2.	.....	60

INTRODUCTION

At the current stage in the development of the chemistry of the fluorocarbons and their derivatives, it is highly desirable to enlarge and expand the knowledge of the fluorocarbon carboxylic acids and their related compounds. Toward this end, the specific problem posed to the author and dealt with in the work herein reported is as follows: isolate, establish formula, and characterize as to physical and chemical properties the intermediates in the reactions between the silver salts of the fluorocarbon carboxylic acids and the halogens or halogen-like substances.

The fluorocarbon carboxylic acids have already proven themselves to be valuable starting materials in the synthesis of fluorocarbon derivatives. Their acid chlorides and anhydrides have also been adapted to a number of synthetic methods through modifications of procedures familiar to the organic chemist. In addition, several processes have been developed involving decarboxylation of the metallic salts of these acids, either with or without other materials being present. A knowledge of the nature of the halogen addends of the silver fluorocarbon carboxylates is essential to the explanation of the mechanism of certain reactions of this type and is contributory to the understanding of the general reactions of the fluorocarbon

carboxylic acids and their derivatives. More important, however, is the value of this knowledge in the prediction of entirely new routes to fluorocarbon derivatives hitherto unavailable through the synthetic approaches used in organic chemistry.

The literature contains a number of papers relating to the compounds produced through the interaction of the metallic salts of the organic carboxylic acids with the halogens. There is considerable disagreement as to the nature of the intermediate substances, and many of the conclusions drawn regarding reaction mechanisms appear conjectural. Some reactions of mixtures of the salts of the fluorocarbon carboxylic acids with the halogens have also been investigated. In the development of synthetic procedures involving the use of these mixtures, some investigators have suggested mechanisms apparently based upon some of the earlier conclusions regarding the silver salts of the organic carboxylic acids. The suggested mechanisms involved intermediates which were never isolated or identified and whose existwas purely speculative. In addition, extrapolation from organic to fluorocarbon chemistry has been demonstrated to be, at best, highly hazardous, even when based upon completely substantiated organic data. It was evident that a detailed quantitative investigation should be undertaken in order to eliminate the confusion existing in this area.

The intermediates in the reaction between the silver salts of the fluorocarbon carboxylic acids and the halogens were found, by methods described in the experimental section of this dissertation, to be addendum compounds of the composition $(\Theta COO)_2AgX$ where Θ is a

fluorocarbon radical and X is a halogen. The properties found for these substances serve to demonstrate again both the similarities and the fundamental differences between the conventional organic compounds and the fluorocarbons and their derivatives. Information is provided which is useful in the chemistry of both silver and the halogens. Halogen-like properties of other materials substituted for X in this compound are clarified. The value of these addendum compounds in the synthesis of the derivatives of the fluorocarbons is also demonstrated, in part, in the experimental section of this dissertation.

A number of approaches to the problem of characterizing these intermediates might have been suggested.

The problem could be attacked through purely theoretical methods based on previously-determined thermodynamic data. This approach was discarded since the data necessary to such an investigation were not available.

The molecular structure and configuration of the intermediates might be determined through the use of X-ray diffraction, infrared spectra, and other physical means. This method was also discarded due to the fact that preliminary investigations had indicated that the substances were not adapted to such an approach.

A third possibility was the synthetic approach, involving preparation and isolation of the intermediates under rigorously controlled conditions, followed by their characterization through chemical reaction. This method was adopted since both the information in the literature and that gained through preliminary investigation indicated

that it should be most productive of conclusive results.

Historical background.--With the original preparation and investigation of trifluoroacetic acid by Swarts,[39] it became evident that here was a new series of acids whose characteristics showed every promise of proving to be markedly different from those of their organic analogs. However, only since the development of the Simons electrochemical process[37] have the fluorocarbon carboxylic acids become readily available for research purposes.

Before considering the reactions of the silver salts of these acids with the halogens, the earlier work involving the silver salts of the organic carboxylic acids should be cited.

The first reference in the literature is to the reaction between silver benzoate and bromine. Peligot,[27] in 1836, combined these materials in benzene solution and obtained meta-bromo benzoic acid as a product.

Simonini[35,36] conducted the first extensive investigations into these reactions, using the silver salts in combination with iodine or bromine, and arrived at conclusions which, as far as they went, have found acceptance among most of the subsequent investigators. Simonini reported that the silver salt of a hydrocarbon carboxylic acid reacted with halogen in a 1:1 equivalent ratio, giving a complex of the formula $(RCOO)_2AgI$ and liberating a mole of silver iodide. This complex, he continued, would decarboxylate upon heating, giving esters of the formula RCOOR and liberating carbon dioxide and silver iodide.

Kleinberg,[22] in reviewing the work prior to 1947, concluded

that the products of reactions involving these starting materials depend upon five factors, namely: (1) the nature of the silver salt, (2) the temperature of reaction, (3) the presence or absence of other reactive materials, (4) the nature of the solvent, and (5) the equivalent ratio of silver salt to halogen. Kleinberg states that the reaction appears to fit a definite pattern only when the equivalent ratios of silver salt to halogen are 1:1 or 1:2. According to Oldham and Ubbelohde,[25] however, a third category exists, involving an equivalent ratio of 3:4.

The above-cited work of Simonini falls into the 1:1 group, as does that of Prevost[29-34] who, in a series of papers, elaborated upon the earlier work of Simonini. He described the addition of the complex intermediates to olefinic compounds to give the halogen-containing esters followed by di-esters which could then be hydrolized to give glycols. He contended that the complex first added across the double bond, giving the halogen-containing ester and liberating RCOOAg which then underwent an exchange reaction with the halogen in the ester to produce the di-ester, with the liberation of silver halide. He found that the proportion of di-ester formed was directly dependent upon the solubility of the silver salt in the solvent employed. Prevost also investigated the reaction between the complex and butadiene, and concluded that the addition was 1, 2 rather than the 1, 4 exhibited by halogens. He described the iodinating action of the complex formed with silver benzoate and iodine and refers to the "metallic" character of halogens in such complexes. Prevost confines himself almost

entirely to the use of silver benzoate and iodine as starting materials. Herschberg[19] and Wieland and Fischer[42] also investigated these reactions and arrived at similar conclusions.

The reactions of the silver salts of the dicarboxylic acids with the halogens have been investigated.[4,6,10,42,43,44] Both 1:1 and 1:2 silver salt to halogen equivalent ratios have been employed.

Investigations involving a 1:1 ratio were first carried out by Birnbaum and Gaier,[4] who reacted the salts of malonic, malic, succinic, tartaric, fumaric, and maleic acids with iodine and obtained the corresponding acids or anhydrides, carbon dioxide, and silver iodide. Wieland and Fischer[42] obtained lactones along with the acid or anhydride. Similar results were obtained by other investigators.

When equimolar quantities of halogen are heated with the silver salts of the dicarboxylic acids carbon dioxide, silver halide, and the corresponding di-halide are obtained. For example, Boehemuller and Hoffman[6] obtained 1,4-dibromobutane from silver adipate and bromine.

This second general classification, that involving an equivalent ratio of 1:2, is represented in the work of Birckenback, Goubeau, and Berninger;[3] Boehemuller and Hoffman;[6] and others.[23,26] According to these investigators, an intermediate substance of the formula RCOOX apparently is formed by the following reaction:

$$RCOOAg + X_2 \longrightarrow RCOOX + AgX$$

Upon heating, this material will decarboxylate according to the following equation:

$$RCOOX \xrightarrow{heat} RX + CO_2$$

The work of Bochemuller and Hoffman can be cited as being typical of the investigations involving the 1:2 equivalent ratio. In the process of chlorinating allyl chloride in acetic acid solution, these investigators obtained a dichloro ester by a process for which they postulated the following mechanism:

(1) $CH_3COOH + Cl_2 \longrightarrow CH_3CO_2Cl + HCl$

(2) $CH_3CO_2Cl + CH_2{=}CHCH_2Cl \longrightarrow CH_3CO_2CH_2CHClCH_2Cl$

The intermediate acetyl hypochlorite was never isolated, nor were the corresponding hypobromites or hypoiodites in subsequent investigations by these and other workers. They found that equilibrium (1) could be shifted to the right by the use of a silver salt in preference to the free acid. They found that the reaction mixture would take up another mole of silver salt, with the formation of complexes of the formula $(RCOO)_2AgX$. These are, of course, the previously described Simonini complexes.

Bochemuller and Hoffman[6] describe the thermal decomposition of the acyl hypoiodites as occurring by two paths, one giving the alkyl iodide as above and the second giving the ester by the following reaction:

$$2\ RCOOX \xrightarrow{heat} RCOOR + CO_2 + X_2$$

Upon reacting bromine with silver benzoate in boiling carbon tetrachloride, these investigators obtained bromobenzene in an 80 percent yield. Luttringhaus and Schaede[23] disagreed with these findings, maintaining that the degradation was unsatisfactory.

Bochemuller and Hoffman;[6] Birckenback, Goubeau, and Berninger;[3]

and Uschakov and Tchistov[41] investigated the reactions of the acyl hypohalogenites with olefinic substances.

Birckenback and co-workers[3] reacted the filtrate of the reaction between equimolar quantities of silver acetate and iodine at -80° in ether with cyclohexene. He obtained the acetate of 2-iodo-1-cyclohexanol. Kleinberg[22] states that this is undisputed evidence of the presence of CH_3COOI in solution. These results would seem to indicate that the ester-producing reaction is due to the presence of RCOOX rather than the Simonini complex as was concluded by Prevost.

Carlsohn[9] was able to isolate a substance of the formula RCOO(Py)I from the reaction of pyridine with solutions resulting from the reactions of silver salts with iodine.

Oldham and Ubbelohde[25] characterized a third class of compounds, the iodine triacyls, which were obtained when an equivalent ratio of 3 silver salt to 4 iodine was employed. They postulated the following equation for their production:

$$3\ RCOOAg\ +\ 2\ I_2 \longrightarrow 3\ AgI\ +\ I(OCOR)_3$$

These compounds contain tervalent iodine, as opposed to the univalent positive iodine said to be present in both the Simonini complex and the acyl hypohalogenite. They were able to isolate the iodine triacyls by chilling filtered solutions of the triacyl in carbon tetrachloride or petroleum ether and collecting the material which crystallized on a filter septum. They postulated a number of free-radical mechanisms for the thermal decompositions of these substances and present considerable analytical data in support of their findings. It

appears that the reaction products of the iodine triacyls are not substantially different from those of the Simonini complexes or acyl hypohalogenites.

Oldham[26] was not able to obtain the corresponding bromine triacyls. He investigated the reactions of bromine with monobasic aliphatic acids, monobasic aromatic acids, monobasic aliphatic monoketo acids, dibasic aliphatic acids, and dibasic aromatic acids. His results were similar to those previously obtained by other investigators.

The first investigation into the reactions of the silver salts of the fluorocarbon carboxylic acids was undertaken by Swarts,[40] who reacted silver trifluoroacetate with iodine in benzene solution at 60°. He gives the following equation, which is representative of the overall reaction:

$$2\ CF_3CO_2Ag + 2\ I_2 + 2\ C_6H_6 \longrightarrow (CF_3CO_2)O + H_2O + 2\ AgI + 2\ C_6H_5I$$

Thus, the reaction mixtures of the silver salts of the fluorocarbon carboxylic acids with iodine were demonstrated to possess iodinating power similar to that previously observed in the organic carboxylic acids.

Simons and Brice[38] developed a process for the production of fluorocarbon iodides through the decarboxylation of the silver salt of a fluorocarbon carboxylic acid in the presence of excess iodine in a high-boiling fluorocarbon solvent, and were granted a patent. No attempt was made to postulate a mechanism for this reaction.

Henne and Zimmer[18] investigated the action of mixtures of

silver trifluoroacetate and bromine or iodine on toluene. They found that ring halogenation occurred below 100°, and advanced the following equations for the reaction:

$$CF_3CO_2Ag + X_2 \longrightarrow AgX + CF_3CO_2X$$

$$CF_3CO_2X + CH_3C_6H_5 \longrightarrow CF_3CO_2H + CH_3C_6H_4X$$

In this mechanism, the iodinating entity is the CF_3COOX. They state that the positive halogen "hangs" from a polarizable atom attached to one or two strongly-active methforyl groups.

Haszeldine and co-workers,[11-14] in a series of papers, have reported investigations of the reactions of a number of the salts of the fluorine-containing monocarboxylic acids with the halogens.

In the first of this series, Haszeldine[11] describes the decarboxylation of silver trifluoroacetate in the presence of iodine to give trifluoromethyl iodide. He states that the intermediate in the reaction is CF_3COOI. This substance, he contends, is formed when iodine is taken up by silver trifluoroacetate in a 2:1 equivalent ratio.

In the second of this series, Haszeldine and Sharpe,[12] after obtaining some results somewhat inconsistent with the above postulate, suggest that an equilibrium exists between the hypohalogenite and a Simonini-type complex in which the iodine and the iodine trifluoroacetate are competing for the silver salt.

$$CF_3CO_2Ag + CF_3COOI \rightleftharpoons (CF_3CO_2)_2AgI$$

If a readily iodinated substance, such as phenol, is added, the iodine trifluoroacetate is removed and the proper amount of silver iodide is

precipitated in accordance with the equation cited under the work of Henne and Zimmer.[18]

Haszeldine[12] was unable to isolate either iodine trifluoroacetate or the Simonini complex. He used nitrobenzene as a solvent in the above experiments.

Haszeldine[12] brominated and iodinated a number of aromatic compounds by this method and devoted considerable space to the discussion of ionic and free-radical mechanisms for this and related reactions.

In the third paper in this series, Haszeldine and Sharpe[13] describe the decomposition of the silver salts of the fluorohalogenoacetic acids in the presence of the halogens to give the fluorohalogeno alkyl halide in the same manner as with the fluorocarbon carboxylic acid salts. They also describe the preparation of higher fluorocarbon mono-iodides from the higher acids. They discuss the preparation of methforyl halides by the same reaction, using the potassium or sodium salt as an alternative to the silver salt. A number of miscellaneous reactions and attempted reactions are described.

In the fourth paper in this series, Haszeldine and Jander[14] report the synthesis of fluorocarbon nitro and nitroso compounds by the decarboxylation of the silver salt of acetforic acid in the presence of nitrosyl chloride. They give the following generalized equation for the reaction:

$$CF_3\cdot(CF_2)_nCO_2Ag \xrightarrow{NOCl} AgCl + CF_3\cdot(CF_2)_nCOONO$$

$$CF_3\cdot(CF_2)_nCOONO \xrightarrow{heat} CF_3\cdot(CF_2)_nNO + CF_3\cdot(CF_2)_nNO_2 + CO_2, \text{ etc.}$$

This involves an intermediate which is analogous to the trifluoroacetyl hypohalogenite previously postulated. This intermediate, like the others, was never isolated or characterized. Banus[1] had previously synthesized fluorocarbon nitro and nitroso compounds by another method.

Cady and Kellogg,[7] in an interesting paper, describe the isolation of an unstable substance having the formula CF_3COOF from the reaction of acetforic acid with fluorine in a closed glass system. Menefree and Cady[24] extended this work to the preparation of C_2F_5COOF and C_3F_7COOF. The hypofluorites were detected by explosions which could be initiated in the reactor. Acetforyl hypofluorite and propionforyl hypofluorite were identified through the determination of molecular weights and the analysis of decomposition products.

Thus, the existence of substances of the formula RCOOF has been established. However, the existence of the analogous hypohalogenites of the general formula RCOOX in the reaction mixtures of silver salt with halogen remains to be proved.

PREPARATION, ISOLATION, AND IDENTIFICATION OF THE COMPLEXES

Determination of Extent of Reaction

Discussion.--The stoichiometry of the reaction between the silver salt of a fluorocarbon carboxylic acid (hereafter designated S) and a halogen (X) is of paramount importance, for it provides an essential clue as to the nature of the product formed at temperatures below that of decarboxylation and in the absence of other reactive materials. Thus, if the reaction leads to the formation of a substance of the formula $\theta COOX$ (where θ is a fluorocarbon radical) by a path of the type

$$(S) + X_2 \longrightarrow \theta\,COOX + AgX$$

one mole of (S) should consume two equivalents of X. If the reaction leads to the formation of the fluorocarbon analog of a Simonini complex by a path of the type

$$2\,(S) + X_2 \longrightarrow (\theta COO)_2AgX + AgX$$

one mole of (S) should take up one equivalent of X. If, as Haszeldine subsequently contended, an equilibrium exists of the type

$$(S) + \theta COOI \rightleftharpoons (\theta COO)_2AgI$$

free iodine should be present during the entire process, its color remaining relatively constant or becoming progressively more intense, depending upon the value of K_{eq}. (No values for K_{eq} were provided.)

In order to obtain accurate and reproducible results, a solvent must be employed which can in no way react chemically with the materials under investigation. The solvent should be clear, non viscous, reasonably low-boiling, and capable of dissolving the active intermediate under consideration.

In the preliminary investigations, a number of different common organic solvents were tried and subsequently discarded as failing to meet one or more of the above specifications. Erratic, non-reproducible results could usually be attributed to the occurrence of secondary reactions involving the solvent. Among these are oxidative attack upon the solvent by the intermediate, halogenation of the solvent by the intermediate, hydrolysis of the intermediate by the solvent itself or by traces of water in solvents having a high affinity for water, and secondary complexing between the solvent and (S) or the intermediate.

Ether, chloroform, carbon tetrachloride, and pentane were tested and discarded. Of these, pentane gave the most consistent results, checking closely with those obtained using a solvent consisting of fluorocarbons or their inert derivatives. The results of these preliminary investigations appear in Table 2.

Fluorocarbons, fluorocarbon nitriles, and fluorocarbon cyclic oxides were used as solvents. These materials are ideally suited to this investigation because of their inertness to chemical attack, complete lack of color, low viscosity, and the fact that a particular

solvent could be chosen having a boiling point suited to the experiment being performed. The low solubilities of halogens and (S) in these media do not constitute a serious drawback. The rate of reaction of (S) with X is decreased and becomes partially dependent upon the stirring rate. However, since the investigation is not a study of rate phenomena, this is not a deterrent factor. On the contrary, it is desirable to have the reaction proceed at a reasonable and orderly rate, as contrasted to the violent manner in which it occurs in solvents such as ether, in which both (S) and X are highly soluble.

The solvents consisting of fluorocarbons or their derivatives were subjected to rigorous purification and deactivation before being used in experiments. The procedure for this is described in the experimental part of this section.

The source and purity of the fluorocarbon carboxylic acids and other materials employed in the following investigations are described in Table 1.

Experimental.--Determination of the stoichiometry of the reaction between (S) and X was carried out using the apparatus shown in Figure 1. The silver salts of the fluorocarbon carboxylic acids were prepared by refluxing the acid with excess Ag_2O in aqueous solution, followed by filtration and removal of water under vacuum. The salts were purified by repeated recrystallization from anhydrous ether. Final ether removal and drying was effected by warming in vacuo.

Since the solubility of X in the fluorocarbon solvent is low,

it is impractical to make up the complexes by addition of a standard solution of X to a slurry of (S). The following techniques were adopted.

Iodine (analytical reagent grade) was resublimed through P_2O_5 and collected on a water-cooled coldfinger in the sublimation flask. The apparatus was transferred to the drybox and the iodine removed from the coldfinger and stored in an appropriate container. Samples of the iodine were transferred in the drybox to weighed 3" or 4" test tubes. The tubes were then quickly sealed, using a gas oxygen torch. The tube and contents plus the scrap were weighed on the analytical balance and the net amount of iodine per sample determined.

Analytical reagent grade bromine was dried by distillation from P_2O_5, and weighed samples were made up in the same manner as with iodine.

The following fluorocarbons and fluorocarbon derivatives (hereafter designated CF) were used as solvents:

#1. N and iso-pentforane mixture (C_5F_{12}) -- This material was washed with anhydrous ether for removal of fluorocarbon hydrides, refluxed with KOH, refluxed with CF_3COOAg + I, treated with sodium thiosulfate, dried over $CaCl_2$, and fractionated. The fraction, boiling 29-31°, was taken. The fluorocarbon solvent, thus freed of any impurities which might react with the intermediate, was stored over P_2O_5 in sealed glass tubes.

#2. Nonforane mixture (C_9F_{20}) -- This material was treated as above, and distilled. A rather wide fraction, boiling 118-130°,

was obtained. This was stored over P_2O_5.

#3. Butforyl nitride ($C_{12}F_{27}N$) -- This material was treated as above and used for a solvent in the fluorocarbon mono-iodide synthesis of Simons and Brice.[38] It was distilled; and the fraction, boiling 165-180°, consisting of various isomers was obtained. The material was stored over P_2O_5.

#4. "Fluorochemical 0.75" (a cyclic oxide of the formula $C_8F_{16}O$) -- This material was treated in the same manner as the butforyl nitride, and fractionated. The fraction, boiling 100-101.5°, was stored over P_2O_5.

The procedure used for carrying out controlled reactions of (S) with X under absolutely anhydrous conditions and for determining the stoichiometry of that reaction was as follows: The reactor (Figure 1) was thoroughly dried by alternate evacuation and admission of dry air. A sample of (S), weighed to be somewhat (usually in the vicinity of .1 gram) less than that required for a 1:1 equivalent ratio with one of the previously weighed X samples, was carefully poured into the graduated reactor vessel D. This was accomplished by lowering D a few inches, while maintaining a stream of dry air through the system from L and pouring (S) from the weighing bottle directly into D. Great care was taken to avoid getting any (S) on the inside of the joint. D was replaced and the drying process repeated to remove any water that might have entered the system. The weighing bottle was then reweighed and the net amount of (S) determined.

The vial of X was dropped in through the top while the air stream from the system was maintained. Breakage of the vial could be assured by shooting it in with a sling-shot arrangement attached to the rim of the tube. The solvent was then admitted from B, removing any (S) that might have clung to the sides of D. Magnetic stirring was started, and a reasonable time was allowed for the reaction to go to completion.

If all color was removed, more halogen could be added. If, on the other hand, the characteristic red-brown or red-purple color due to free bromine or iodine remained, enough (S) was added to bring the equivalent ratio up to, or perhaps very slightly in excess of, 1:1. Completion of reaction could then be noted by the disappearance of all color in the solution when this point was reached.

In every case free halogen remained until additional (S) was added, after which a few minutes' stirring removed all trace of color. The numerical data pertaining to these experiments appear in Table 3.

Thus it is demonstrated that bromine and iodine are consumed quantitatively to the 1:1 equivalence point, and that immediately after passing that point the color of free halogen is evident. Next it is desirable to determine if the amount of free halogen remains relatively constant as X is added, due to the establishment of an equilibrium of the type cited under the work of Haszeldine, or whether all the halogen added past the end point is present in the free state. Only one unassailable method for such an experiment appears to exist. That is to bring a mixture of (S) and X_2 to the 1:1 equivalence point and then to

add known quantities of standard X solution past that point. A sample of the same solvent not containing any reactant materials (hereafter referred to as the blank) is then titrated with the same X solution to the point at which its color matches that of the above solution containing the reactants. The ratios of added solution to original solvent in the reaction mixture are compared to the corresponding ratios in the blank at the point at which the colors are observed to match. Thus, if all halogen added to the reaction mixture in excess of the 1:1 stoichiometric point is present in the free state, the values for these ratios should coincide at each point of identical color intensity. The tabulated values for the above ratios appear in Table 4. The degree to which they coincide as successive amounts of iodine-containing solvent are added is evident.

A saturated solution of I_2 in "Fluorochemical 0.75" (solvent #4) was prepared and standardized against thiosulfate. The violet solution had a normality of only .00134.

AgI was prepared from $AgNO_3$ and KI and dried by warming in vacuo in the absence of light. This was to be added to the blank in order to provide identical visual conditions. However, it was discovered that AgI itself is capable of removing small quantities of iodine from solution. The extent of this phenomenon was measured by titrating 2.5074 g. AgI in 10 cc. of #4 solvent with the standard iodine solution. At 65 cc. a noticeable pink color appeared. Thus, the AgI decolorizes I_2 in a 121 to 1 equivalent ratio of AgI to I_2 in the ~~CF~~ solvent.

The experiment was repeated using reagent grade nitrobenzene. A .026 N solution of iodine in this solvent was prepared and standardized against thiosulfate. A suspension of 4.3059 g. AgI in 10 cc. pure nitrobenzene decolorized 14.90 cc. of I_2 solution. Detection of color change is difficult in a colored solvent such as nitrobenzene; hence the I_2 solution was added until the color was obvious. The nitrobenzene solution was then filtered and back-titrated with .5 cc. of .1000 N thiosulfate to a starch end-point. The AgI was found to decolorize I_2 in a 54 to 1 equivalent ratio of AgI to I_2 in nitrobenzene.

This phenomenon, though small, is just another of the complicating factors which can lead to erroneous results, if not properly recognized.

The experiments were conducted using an amount of AgI in the blank proportional to that which would be produced by the complex-forming reaction.

The color-change characteristics of free iodine in OF solvents, plus the extreme dilution of the solution used, enabled this investigator to make measurements of high precision with a minimum of human error. The results obtained were in remarkably close agreement with theory.

Results of the above measurements.--The object of these measurements has been to establish the stoichiometry of the reaction of (S) with X. This was accomplished through the addition of X to (S) in a OF solvent and observation of the point in the addition at which free halogen appeared and the manner in which the color intensity increased

past this point. Similar results were obtained for (S) from silver trifluoroacetate through silver valerforate and for bromine and iodine. It was demonstrated that after the 1:1 equivalence point is reached in the addition of X to (S), free halogen appears in what had been, up to this point, a colorless solution. Furthermore, the deepening of the color as I_2 was added past this point progressed linearly with the addition of I_2, paralleling the color intensity deepening of a simultaneously-run blank.

It was therefore demonstrated that when the reaction is carried out at temperatures below that at which decarboxylation can occur, in a completely inert solvent, and under strictly anhydrous conditions, the reaction occurs in a 1:1 equivalent ratio and that any halogen added in excess of this is present only in the free state.

The latter measurement was conducted using iodine only. Similar color deepening past the end point was observed with bromine, but the color characteristics of bromine in the solvent used and the high volatility of bromine (resulting in its escaping from solution into the air space above) prevented precision observation of color change.

Some of the investigators have arrived at conclusions as to the extent of the reaction by weighing as AgX the precipitate obtained at various stages during the halogen addition. This involves the erroneous assumption that all the material precipitating during the reaction is silver halide. It will be shown that the precipitated material is, in reality, a mixture of AgX and $(RCOO)_2AgX$. The proportion of the latter in the precipitate is inversely proportional

to its solubility in the solvent employed. Then, when the mixed precipitate is removed from the reaction mixture by filtration, and presumably washed and dried prior to weighing, the $(\theta COO)_2AgX$ is converted to AgX, $AgXO_3$, and free acid by a reaction of the type

$$(\theta COO)_2AgX + H_2O \longrightarrow 2\ \theta COOH + AgOX$$

followed by

$$3\ AgOX \longrightarrow 2\ AgX + AgXO_3$$

as will be shown in the following section.

The danger of confusion is further increased by the great similarity in appearance between AgX and the mixture AgX + $(\theta COO)_2AgX$. In the preliminary experiments (see Table 2) and in subsequent investigations, (S) was stirred with I_2 under anhydrous conditions and in the absence of a solvent. A yellow, amorphous powder resulted, having the overall composition $\theta COOAgI$. This material cannot be visually distinguished from AgI. The addition of iodine in excess of the 1:1 equivalent ratio produces the red-purple color of the free halogen.

The phenomenon of iodine absorption by silver iodide, though small, is still a complicating factor. It was demonstrated to be over twice as large in nitrobenzene as in "Fluorochemical 0.75."

TABLE 1

SOURCE AND PURITY OF MATERIALS USED IN THE INVESTIGATIONS HEREIN REPORTED

Compound	Source	Purity	Further Purification
Acetforic acid	M. M. & M. Co.	95-98%	fractionation
Propionforic acid	M. M. & M. Co.	90-95%	fractionation
Butyrforic acid	M. M. & M. Co.	75-85%	fractionation
Valerforic acid	M. M. & M. Co.	95-98%	fractionation
Caproforic acid	M. M. & M. Co.	90-95%	fractionation
Bromine	Mallinckrodt	Anal. R.	described on p. 16
Iodine	Mallinckrodt	Anal. R.	described on p. 16
Pyridine	Mathieson	U.S.P.	fractionation and drying
Pyridine	Eastman Kodak (DPI)	Spectral Grade	drying
Phosphorus (red)	Mallinckrodt	Tech.	dessication
M-di isopropyl benzene	Dow	Tech.	fractionation
2-butyl benzene	Koppers	Tech.	fractionation
Silver oxide	Fischer	C.P.	------

TABLE 2

PRELIMINARY EXPERIMENTS DETERMINING THE STOICHIOMETRY OF REACTION OF SILVER ACETFORATE WITH IODINE OR BROMINE IN VARIOUS SOLVENTS

(S)	g.	M.Eq.	X	g.	M.Eq.	Solvent	Reaction Time	Temperature & Conditions	Extent of Reaction
CF_3COOAg	55	250	I_2	63	500	GF mixt. BP-170 250 cc.	7 days	25° - 100° tube-shaking	incomplete
CF_3COOAg	60	270	added to above reaction mixture				12 hours	25° - 35° tube-shaking	complete
CF_3COOAg	22.1	100	I_2	25.4	200	GF mixt. BP-170 100 cc.	10 days	25° - 100° tube-shaking	incomplete
CF_3COOAg	6.8	30.7	I_2	3.89 (approx)	30.7 (approx)	$CHCl_3$ 32 cc.	15 min.	26° - 27° tube-shaking	complete
CF_3COOAg	11.5764	52.38	I_2	6.4799	51.02	CCl_4 47 cc.	12 hours	24° - 26° stirring	incomplete
CF_3COOAg	13.8905	62.48	Br_2	9.3254	11.65	ether 120 cc.	instan-taneous	24° - 38° stirring	complete
CF_3COOAg	2.6689	12.07	I_2	1.9151	15.08	ether 57 cc.	reacted as titrated	26° - 27° stirring	end-point vague
CF_3COOAg	2.3360	10.57	I_2	2.5071	19.82	ether 48 cc.	reacted as titrated	25° - 27° stirring	93% of 2:1

TABLE 2--Continued

(S)	g.	M.Eq.	X	g.	M.Eq.	Solvent	Reaction Time	Temperature & Conditions	Extent of Reaction
CF_3COOAg	7.6649	34.6	Br_2	4.6136	57.67	ether 89 cc.	reacted as titrated	26° - 27° stirring	83% of 2:1
CF_3COOAg	3.2031	14.04	Br_2	1.8619	11.65	ether 53 cc.	15 min.	24° - 25° stirring	incomplete
C_3F_7COOAg	14.0801	43.8	I_2	5.5533	43.9	pentane 100 cc.	30 min.	25° - 26° stirring	complete
C_3F_7COOAg	10.3668	32.29	I_2	4.5029	35.45	pentane 100 cc.	5 hours	25° - 27° stirring	incomplete
C_3F_7COOAg	1.2046	3.75	added to above reaction mixture				2 min.	25° - 26° stirring	complete

TABLE 3

THE STOICHIOMETRY OF THE REACTION OF SILVER SALTS OF FLUOROCARBON CARBOXYLIC ACIDS WITH IODINE OR BROMINE IN FLUOROCARBON SOLVENTS

	(S)	g.	M.Eq.	X	g.	M.Eq.	Solvent	Reaction Time	Temp. °C	(S)/X Equiv. Ratio	Extent of Reaction
1.	CF_3COOAg	28.0	126.7	I_2	16.0	126.00	#3 250 cc	3 hrs	25-27	.995	complete
	----	same	---	I_2	.20	1.57	same	2 hrs	25-26	1.007	incomplete
2.	C_3F_7COOAg	5.0772	15.81	I_2	2.3148	18.23	#3 30 cc	2 hrs	25-26	1.153	incomplete
	C_3F_7COOAg	.8081	2.52	--	same	---	same	10 min	25-26	.995	complete
3.	CF_3COOAg	4.6033	20.83	Br_2	1.8668	23.36	#1 25 cc	6 hrs	24-26	1.121	incomplete
	CF_3COOAg	.5675	2.57	--	same	---	#1 25 cc	18 hrs	24-26	.998	complete
4.	C_3F_7COOAg	25.54	79.5	I_2	10.858	85.6	#3 150 cc	15 hrs	23-25	1.07	incomplete
	C_3F_7COOAg	2.00	6.2	--	same	---	same	15 min	23-25	.999	complete
5.	$C_5F_{11}COOAg$	42.00	99.8	I_2	17.00	133.9	#2 220 cc	24 hrs	24-26	1.33	incomplete
	$C_5F_{11}COOAg$	15.80	37.5	--	same	---	same	3 hrs	24-26	.969	complete
6.	CF_3COOAg	8.6418	39.10	Br_2	3.7293	46.67	#3 150 cc	6 hrs	24-26	1.193	incomplete
	CF_3COOAg	1.933	8.74	--	same	---	same	6 hrs	24-26	.975	complete

NOTE: In the second part of each of the six experiments shown, an additional amount of the indicated reactant was added to the reaction mixture.

TABLE 4

MEASUREMENT OF EXCESS IODINE PRESENT IN SOLUTIONS OF REACTION MIXTURES BY THE COLOR COMPARISON METHOD

REACTION MIXTURE				BLANK			
Contents	Stirring Time	cc. Soln. Added	Ratio (R) $\frac{\text{titer}}{\text{solv.}}$	Contents	cc. Soln. Added	Ratio (B) $\frac{\text{titer}}{\text{solv.}}$	$\frac{B}{R}$
CF_3COOAg, 1.103 g. (4.99 M.Eq.)	20 min.	25	.500	AgI, .34 g.	14.00	.700	1.22
	20 min.	25	1.00		9.60	1.18	1.18
I_2, .6323 g. (4.99 M.Eq.)	20 min.	25	1.50	GF, 20.00 cc.	9.25	1.64	1.09
	20 min.	25	2.00		10.05	2.14	1.07
GF, 50.00 cc.	20 min.	25	2.50		8.64	2.58	1.03
CF_3COOAg, .5437 g. (2.46 M.Eq.)	20 min.	25	.500	AgI, .28 g.	12.05	.602	1.20
	20 min.	25	1.00		9.00	1.05	1.05
I_2, .3124 g. (2.46 M.Eq.)	20 min.	25	1.50	GF, 20.00 cc.	9.60	1.53	1.02
	20 min.	25	2.00		10.10	2.04	1.02
GF, 50.00 cc.	20 min.	25	2.50		9.28	2.49	1.00
C_2F_5COOAg, 1.4171 g.(5.23 M.Eq.)	30 min.	25	.500	AgI, .614 g.	9.90	.495	.99
	20 min.	25	1.00		10.45	1.01	1.01
I_2, .6641 g.(5.23 M.Eq.)	20 min.	25	1.50	GF, 20.00 cc.	10.65	1.55	1.03
	20 min.	25	2.00		9.60	2.03	1.01
GF, 50.00 cc.	20 min.	25	2.50		9.25	2.49	1.00
C_3F_7COOAg, 1.0073 g.(3.13 M.Eq.)	30 min.	25	.500	AgI, .36 g.	9.50	.475	.95
	20 min.	25	1.00		10.25	.985	.98
I_2, .3986 g.(3.14 M.Eq.)	20 min.	25	1.50	GF, 20.00 cc.	10.55	1.51	1.01
	20 min.	25	2.00		10.00	2.02	1.01
GF, 50.00 cc.	20 min.	25	2.50		9.85	2.51	1.00

TABLE 4--Continued

Contents	Stirring Time	cc. Soln. Added	Ratio (R) titer / solv.	Contents	cc. Soln. Added	Ratio (B) titer / solv.	B / R
C_4F_9COOAg, 2.2482 g. (6.06 M.Eq.)	45 min.	25	.500	AgI, .50 g.	10.00	.500	1.00
	20 min.	25	1.00		10.50	1.05	1.05
I_2, .7694 g. (6.06 M.Eq.)	20 min.	25	1.50	$\mathfrak{GF}$, 20.00 cc.	10.10	1.53	1.02
	20 min.	25	2.00		9.40	2.00	1.00
$\mathfrak{GF}$, 50.00 cc.	20 min.	25	2.50		10.33	2.52	1.01
$C_5F_{11}COOAg$, 2.5829 g.(6.13 M.Eq.)	45 min.	25	.500	AgI, .50 g.	10.00	.500	1.00
	20 min.	25	1.00		9.01	.951	.95
I_2, .7791 g.(6.13 M.Eq.)	20 min.	25	1.50	$\mathfrak{GF}$, 20.00 cc.	10.41	1.47	.98
	20 min.	25	2.00		10.05	1.97	.99
$\mathfrak{GF}$, 50.00 cc.	20 min.	25	2.50		9.63	2.46	.99

KEY TO FIGURE 1

A. Drying tube

B. Burette

C. Manometer #1

C'. Manometer #2

D. Graduated reactor vessel

E. Magnetic stirrer

F. Stopcock

G. Filter-weighing bottle

H. Trap

I. Saran flex joint #1

I'. Saran flex joint #2

J. Trap

K. Stopcock

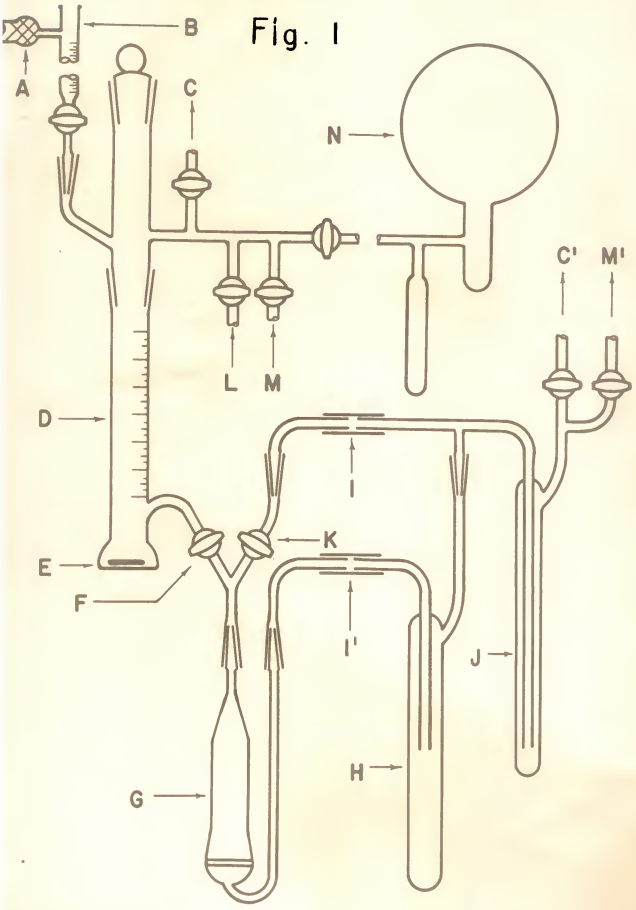
L. Dry-air supply

M. Vacuum

M'. Vacuum

N. 5-liter gas bulb

Fig. 1



Analysis of Reaction Mixtures

Discussion.--Further information as to the nature of the halogen addends of the silver fluorocarbon carboxylates can be obtained through the analysis of the reaction mixtures for total oxidizing power and recoverable acid.

A comparison is made between the total available oxidizing power for the complexes formed with silver acetforate through silver caproforate and bromine or iodine. From these data important conclusions as to the formulae and properties of the complexes may be drawn.

Recoverable acid is important from the standpoint of determining whether or not all the (S) is consumed in the reaction forming the readily hydrolizable complex. Also, it serves to determine the extent of side reactions such as decarboxylation, which could eliminate acid from the system. The extent of the occurrence of the decarboxylation reaction, if any, was also checked by the observation of any pressure changes occurring in the system during the initial reaction and by measuring the weight increase of an ascarite tube attached to the system, as shown at M in Figure 1. No appreciable pressure rise or weight change could be detected for iodine, although the bromine reaction did give some evidence of gas evolution.

In a few cases, recoverable silver was determined as a check on the analytical method to be used in subsequent determinati ns of the silver content of the purified solutions and isolated complexes, in which this factor is highly critical.

Experimental.--The reactions were conducted as before, using the apparatus in Figure 1 and a CF solvent.

Total oxidizing power was determined by adding KI to the colorless reaction mixture, shaking until the reaction appeared complete, adding water, and immediately titrating the liberated iodine with standard thiosulfate.

Liberated acid was determined on separate reaction mixtures by treatment with water, followed by titration with standard base to a phenolpthalein end point. In other cases, a considerable excess of (S) was employed. The acidic solution resulting upon the addition of water was distilled into a closed receiver. More water was added and the process repeated until all the free acid was obtained. This was then titrated to a phenolpthalein end point with standard base.

Recovered silver was determined by the Deniges cyanide method.

Experimental data and analytical results appear in Table 5.

Results of the above measurements.--The results obtained lead to the following conclusions:

(1) In the case of both bromine and iodine, one equivalent of oxidizing power is available for each equivalent of halogen consumed.

(2) The total oxidizing power is somewhat low for the reaction mixture of silver acetforate and X, but closely approaches the theoretical value as the molecular weight increases.

(3) The reaction time for (S) with X appears to increase with molecular weight of (S) and in going from Br_2 to I_2.

(4) When the total acid, both liberated and present as the

silver salt, was titrated in the reaction mixture, an equivalent of acid was found for every equivalent of (S) originally present. In cases in which the original excess of (S) was large, AgOH was precipitated due to the reaction of the excess Ag ion in solution with the titrating base. However, when the liberated acid was distilled from the mixture in order to separate it from the unreacted (S), one equivalent of acid was found in the distillate for each equivalent of X originally present in the reaction mixture. Thus, the acid liberated from the reaction mixture upon hydrolysis with water is independent of the amount of (S) present in excess of the 1:1 equivalent ratio.

(5) In several instances the precipitate obtained upon treatment of the reaction mixtures with water was separated, washed, and vacuum dried. This precipitate was observed to possess oxidizing power when treated with KI solution. The precipitate was presumed to contain $AgIO_3$.

(6) In every case the precipitate obtained did not seem to be as subject to decomposition by light as is AgX obtained by more conventional methods. Samples of the precipitate obtained after treatment of the reaction mixture were washed and vacuum dried. These were then analyzed according to the Deniges cyanide method and were found in every case to be almost pure AgX.

From the above findings, the equation for the reaction of the complex with KI may be written

$$(\text{OCO})_2\text{AgX} + 2\ \text{KI} \longrightarrow \text{AgX} + 2\ \text{OCOK} + \text{I}_2$$

while the reaction with water may be written as before, i. e.,

$$(\text{OCO})_2\text{AgX} + \text{H}_2\text{O} \longrightarrow \text{AgOX} + 2\ \text{OCOH}$$

$$3\ \text{AgOX} \longrightarrow 2\ \text{AgX} + \text{AgXO}_3$$

TABLE 5

PREPARATION AND ANALYSIS OF REACTION MIXTURES OF SILVER SALTS OF FLUOROCARBON CARBOXYLIC ACIDS AND IODINE OR BROMINE

A. Preparation

(S)	g.	M.Eq.	X	g.	M.Eq.	Solvent	cc.	Mean Temp. °C	Reaction Time (Min.)
CF_3COOAg	1.098	4.97	I_2	.6305	4.96	OF # 2	11	25	90
CF_3COOAg	1.480	6.69	I_2	.8248	6.49	OF # 2	12	26	90
C_2F_5COOAg	2.558	9.44	I_2	1.1086	8.73	OF # 3	20	24	300
C_3F_7COOAg	2.7140	8.45	I_2	1.0259	8.08	OF # 3	15	26	480
C_4F_9COOAg	4.8305	13.0	I_2	1.5945	12.55	OF # 3	30	25	600
$C_5F_{11}COOAg$	2.3930	5.66	I_2	.6908	5.439	OF # 3	30	27	840
$C_5F_{11}COOAg$	3.2500	7.71	I_2	.9105	7.17	OF # 3	37	26	360
CF_3COOAg	1.6452	7.444	Br_2	.5916	7.404	OF # 2	40	25	480
CF_3COOAg	10.5751	47.84	Br_2	3.7293	46.67	OF # 3	150	26	480
C_3F_7COOAg	1.9888	6.195	I_2	.7343	5.782	OF # 4	75	25	300
C_3F_7COOAg	1.8218	5.675	I_2	.6975	5.492	OF # 4	75	26	300

TABLE 5--Continued

B. Analysis

Total Oxidizing Power		Recovered Acid			Recovered Ag		
			% of Theory Based on			% of Theory Based on	
M.Eq.	% of Theory	M.Eq.	Orig. X	Orig. Ag	M.Eq.	Orig. X	Orig. Ag
4.1168	83.00				4.92	98.9	98.8
5.3487	82.41						
7.9459	91.02						
7.6461	94.5				8.36	103	98.9
12.0355	95.1						
4.9798	91.5						
		7.68	107	99.6	7.45	104	96.6
5.6810	76.7				7.13	96.4	95.7
		45.44 (distilled)	97.3	95.0			
		5.55 (distilled)	96.0	89.6	6.18	107	99.6
		5.52	100	97.3	5.61	102	98.9

Analysis of the Complexes in Solution

Discussion.--In the following series of experiments, clear solutions of the complex in the ØF solvent are analyzed for the same quantities determined for the entire reaction mixtures in the previous section. The complicating factors due to precipitated AgI, unreacted (S), and undissolved complex are eliminated. The acid number, total oxidizing power, and recoverable silver are obtained as functions of the amount of complex present in solution.

Since the complexes are only partially soluble in the ØF solvent, the greatest significance will be in the comparative values of the three measured quantities. After the samples of solution are removed, the residual solution and precipitated mixture can be titrated and the summation of all the quantities compared to the theoretical totals.

If the formula for the complex is $(\text{ØCOO})_2\text{AgX}$, and if its reactions with KI and H_2O are represented by the previously-cited equations, then the total oxidizing power in equivalents should equal the acid number, while the recoverable silver should be one half that value.

Also included in these experiments are two designed to determine the relative stability of solutions of the complexes containing bromine as compared to those containing iodine.

Observations of the behavior of the complexes of bromine have indicated that they are less soluble in the solvents employed, and that the solutions are less stable, losing their measurable activities

if allowed to stand for any period of time.

Total oxidizing power was chosen as the parameter for the measurement of the stability of $(\phi COO)_2AgBr$ in solution, since this quality has been demonstrated to be reasonably dependable and independent of excess (S).

Experimental.--The complexes were prepared as before, using the apparatus in Figure 1 and several of the different fluorocarbon solvents. As soon as the reaction was complete, the precipitate was allowed to settle until no particles remained suspended in the clear supernatant liquid.

A special pipette was constructed with a stem sufficiently long to reach into the apparatus from the top and remove 10 cc. samples. A tiny chamber containing calcium chloride was sealed into the stem to eliminate the possibility of contamination of the solution by the operator. The lower end was further constricted to prevent loss of the dense, non-viscous solution during transfer.

The pipette was dried by passing a stream of dry air through it. The top was removed from the reactor, while maintaining a stream of dry air from L. The pipette was partially inserted and allowed to remain suspended in the air stream for a few minutes to remove water from its outside surface. It was then lowered into the supernatant liquid and the sample obtained. The pipette and sample were then removed, the sample rapidly transferred to an erlenmeyer flask and titrated immediately. This process was repeated until the solution level was too low to permit removal of samples without the danger of

their being contaminated with precipitated material from the bottom of the reactor. In the last two experiments a measured time was allowed between removal of samples for titration. The reactor vessel D was then removed and the remaining material titrated directly in the vessel. Experimental and analytical data appear in Table 6. In Part A of this table, values for oxidizing power, liberated acid, and recovered silver for samples removed from reaction mixtures as described above are tabulated. In Part B, values of total oxidizing power for samples removed from reaction mixtures at measured time intervals are tabulated. The time variation of this value for samples of solutions containing $(C_2F_5COO)_2AgI$ and $(C_2F_5COO)_2AgBr$ may be compared.

Results of the above measurements.--The tabulated experimental data and results clearly indicate that the theory cited on page 33 is accurate and that the complexes in solutions separated from precipitated material react with water and KI in accordance with the suggested equations.

The complexes formed with iodine are evidently quite stable in solution, since no marked decrease was noted in the measured quantities during the period of measurement.

On the other hand, the solutions of complexes of bromine rapidly lose their oxidizing power on standing. Furthermore, their initial solubilities in the solvent are somewhat lower than those of the iodine complexes.

For these and other reasons, iodine was used more frequently than bromine in the foregoing and following measurements.

TABLE 6

ANALYSIS OF THE COMPLEXES IN SOLUTION IN FLUOROCARBON SOLVENTS

A. Relationship Between Acid Number, Oxidizing Power, and Removeable Silver

Contents of the Reaction Mixtures	Sample (cc.)	Oxidizing Power (M.Eq.)(O)	Acid No. (M.Eq.) (A)	Recoverable Ag. (M.Eq.) (R)	(R) / (O) or (A)
1. CF_3COOAg, .8347 g. (3.76 M.Eq.)	10	.00993	insufficient material in solution for measurement		
	20	.01986			
I_2, .4245 g. (3.34 M.Eq.)	10	.00993			
	residue	3.1744		3.729	1.17
QF #2, 65 cc.	total	3.2141		3.729+	1.16+
2. C_3F_7COOAg, 1.0600 g. (3.30 M.Eq.)	10		.3009	.1477	.491
	10	.2976		.1454	.489
I_2, .4114 g. (3.23 M.Eq.)	10	.2857		.1498	.524
	10	.2877		.1487	.522
QF #3, 65 cc.	10	.2858		.1436	.502
	residue	1.2598		2.6869	2.13
	total	2.2726		3.3224	1.46
3. $C_5F_{11}COOAg$, 1.71 g. (4.06 M.Eq.)	10	.0516		.0226	.438
	10	.0506		.0240	.475
I_2 .4740 g. (3.732 M.Eq.)	10		.0528		
	10		.0528		
QF #3, 65 cc.	residue	3.3067		3.7296	1.128
	total	3.5460		3.9374	1.109

NOTE: In obtaining totals for oxidizing power and recoverable silver, appropriate values are substituted for those not determined.

TABLE 6--Continued

B. Comparison of Stabilities of Complexes in Solution

Contents of the Reaction Mixtures		Sample (cc.)	Oxidizing Power (M.Eq.)	Age of Sample (Min.)
4. C_2F_5COOAg,	.9868 g. (3.641 M.Eq.)	5	.3050	15
		5	.2910	633
I_2,	.4471 g. (3.520 M.Eq.)	5	.2950	1008
		residue	2.6170	
QF #4,	65 cc.	total	3.5080	
5. C_2F_5COOAg,	1.4121 g. (5.211 M.Eq.)	10	.4010	10
		10	.2650	130
Br_2,	.3987 g. (4.987 M.Eq.)	10	.1830	250
		10	.1400	370
QF #4,	120 cc.	10	.1010	490
		10	.0050	1330
		residue	3.5350	
		total	4.6300	

Isolation of the Solid Complexes

Discussion.--The problem of isolating the solid complexes from their solutions was not easily solved. It was necessary to obtain solutions absolutely free of precipitated AgI and $(\theta CO0)_2AgI$, and to devise a method for separating the complex from the solvent without decomposing it in the process. The entire operation would, of course, have to be carried out under strictly anhydrous conditions.

A number of attempts to remove the solvent from the complex by distillation were made. This invariably resulted in the decomposition of the complex, even when the distillations were carried out under vacuum.

It was discovered that when clear solutions of the complex in a low-boiling CF solvent were chilled to -78°, white crystals precipitated. These were presumed to be the complex, and the apparatus (Figure 1) was adapted to effect their separation by this method. The complexes, thus removed by crystallization and filtration, were weighed and analyzed for total oxidizing power, acid equivalent, and recoverable silver.

Experimental.--The entire apparatus was very carefully dried by alternate evacuation and admission of dry air. The complexes were prepared by the previously-described method, employing as a solvent the low-boiling fluorocarbon mixture (#1). During the preparation of the complex, carried out in the flask designated D in Figure 1, the remainder of the system was subjected to more rigorous vacuum drying, with special attention being paid to the filter-weighing bottle G.

The latter was specially constructed, using a "fine" grade sintered-glass disc as the filter. It was designed to be sufficiently light for use as a weighing bottle (weight 55.4701 g.) and sufficiently compact to fit inside a 1-liter dewar; yet it had a capacity of 42 cc., which enabled it to hold enough solution to assure that a measurable amount of complex could be obtained. It was connected to the system by means of 10/30 standard taper joints, as shown in the diagram. Teflon plugs were provided for insertion in the inside of the male joints on the bottle during the weighing process.

After the reaction had reached completion, the precipitate was allowed to settle. G was chilled in dry ice-acetone. Stopcock F was then opened and the solution allowed to pass into G. Trapped air in G was vented by opening stopcock K. Any suspended particles were removed from the solution by a glass-wool plug in the line between D and F.

After sufficient time had been allowed for crystal formation, suction was applied by opening stopcock M'. The solvent was drawn from the filter-weigh bottle, leaving the precipitated complex on the septum. The solvent was collected in dry-ice trap H or liquid-air trap J.

Since the solution had been removed from D, the stopcock K could be opened and a stream of air allowed to pass through G, removing any remaining solvent.

K was then closed. The dewar containing dry ice-acetone was removed from G and pumping continued one or two minutes while allowing the filter-weighing bottle to warm slightly. This was to assure

complete removal of the solvent. The stopcock K was opened, pumping stopped, and G removed from the apparatus. The teflon plugs were inserted, stopcock grease removed from the joints, and the bottle weighed on the analytical balance.

After this, the contents of the bottle could be titrated either for acid or for total oxidizing power. The titrations were performed directly in the filter-weighing bottle, using a micro burette.

The precipitated silver residues were then washed free of titrating solution. The samples which had been titrated for available acid were treated with a small amount of thiosulfate solution to reduce any $AgIO_3$ to AgI.

Excess standard KCN solution was added and the bottle stoppered and allowed to stand with occasional shaking until all the AgI was dissolved. The solution was then transferred to an erlenmeyer flask and titrated with standard silver nitrate according to the Deniges method.

Experimental conditions and results appear in Table 7. In this table the experimental data relating to the preparation of the complex to be isolated is tabulated, along with the amounts of complex isolated in each case. Values for oxidizing power, acid number, and recovered silver are tabulated. The corresponding theoretical values are also listed for comparison.

Results of the above measurements.--The elusive intermediates in the reaction between (S) and I_2 have been isolated and identified. Their formula has been shown to be $(OCOO)_2AgI$. The technique for their separation and analysis has been described. The corresponding

complexes for bromine were not isolated.

$(\theta COO)_2AgI$, though evidently quite stable in solution, is prone to decomposition when removed from the solvent. The complexes were isolated at -78° as white crystals which rapidly took on a yellow-brown cast when warmed to room temperature. Evidently the occurrence of partial or total decomposition of the complex is marked by this color change, since in early experiments when the complex was allowed to warm to room temperature during the latter part of the separation prior to weighing, the silver content was high in comparison to the acid equivalent. In these cases the precipitate had developed the yellow color.

It can then be concluded that the complex exists as the stoichiometric entity $(\theta COO)_2AgI$ only in solution or at reduced temperatures.

The fact that the precipitated mixture of $(\theta COO)_2AgX$ and AgX is stable, retaining its oxidizing power over long periods of time, and that equivalent mixtures of (S) and X combined in the absence of a solvent produce the observed homogeneous yellow powder which is stable in the absence of moisture or reducing agents, would indicate that the complex is stabilized by the presence of an additional mole of AgX with the formation of a material of the stoichiometric formula $\theta COOAgX$ which resists addition of further X.

TABLE 7

PREPARATION, ISOLATION, AND ANALYSIS OF THE SOLID COMPLEXES

PREPARATION						ANALYSIS						
(S)	g.	M.Eq.	I_2, g.	M.Eq.	Solvent, cc.	Weight of Ppt., g.	M.Eq. Oxidizing Power		M.Eq. Acid Number		M.Eq. AgI	
							Found	Theor.	Found	Theor.	Found	Theor.
C_3F_7COOAg	2.400	7.47	.9418	7.41	#1 50	.4504	.2807	1.362			.2285	.6813
CF_3COOAg	1.5308	6.926	.8778	6.912	#1 50	.1757	.6490	.7622			.3937	.3811
C_2F_5COOAg	1.4233	5.253	.6471	5.095	#1 65	.2560			.8659	.9126	.4613	.4563
C_3F_7COOAg	2.9342	9.140	1.1378	8.959	#1 50	.2125	.6220	.6420			.3198	.3210
C_4F_9COOAg	2.5466	6.864	.8674	6.829	#1 65	.1989			.5001	.5230	.2600	.2615
$C_5F_{11}COOAg$	3.2135	7.633	.9390	7.394	#1 65	.2360	.5320	.5466			.2730	.2733

USES OF THE COMPLEXES IN THE SYNTHESIS OF FLUOROCARBON DERIVATIVES

General Discussion

Mixtures of (S) and X have been found to be capable of halogenating aromatic substances. Haszeldine and Sharpe[12] and Henne and Zimmer[18] have investigated this reaction. Earlier investigators arrived at similar conclusions when investigating the reactions of the silver salts of the ordinary carboxylic acids.

While the present writer cannot, in view of the above-cited findings, agree with the mechanisms advanced by Haszeldine and Henne and their co-workers, it was decided that further investigation into the reaction to clarify more thoroughly all the factors involved should not be undertaken at this time.

The overall equation for the reaction may be written:

$$\text{RCOOAg} + X_2 + \text{ArH} \longrightarrow \text{RCOOH} + \text{AgX} + \text{ArX}$$

The above investigators have demonstrated this to be a highly useful and selective means of obtaining ring-halogenated aromatic compounds.

The reactions involving decarboxylation of (S), either with or without other materials being present, are discussed in the introduction.

When equivalent quantities of (S) and X are mixed in the presence of a solvent and the mixture heated to 120-150°, CO_2 is

evolved; and a mixture of products is formed, consisting of the fluorocarbon mono-iodide, the fluorocarbon carboxylic acid anhydride, and a small amount of straight-chain fluorocarbon (usually containing twice the number of carbon atoms as the original fluorocarbon radical in the starting material).

When an excess of halogen is present, the reaction proceeds toward the formation of almost 100 percent halide by the previously-cited overall reaction

$$\text{RCOOAg} + X_2 \longrightarrow CO_2 + AgX + \text{RI}$$

Although mechanisms involving the complex $(\text{RCOO})_2AgX$ might be postulated for reactions of this type, the present writer feels that nothing would be gained through the suggestion of such mechanisms without the confirmatory evidence which could be gained only through a kinetic study of each process for which mechanisms are advanced.

One immediately is struck by the possibility of substituting other elements or functional groups for the halogen involved in the complex, or substituting other elements or compounds for the second equivalent of halogen whose presence in the reaction mixture makes possible high yields of fluorocarbon halides. The manner in which the decarboxylation would proceed in the presence of these substitute ingredients presents an intriguing problem to the investigator. Much of the following experimental work can be classified under this heading.

The ability of the Simonini complexes to add to olefinic substances with the formation of halo-esters followed by di-esters, as

previously described under the work of Prevost,[30] suggests an interesting line of investigation. Reasoning by analogy (an admittedly hazardous procedure), one could suggest that a reaction of the following sort might occur

$$(\text{RCOO})_2\text{AgX} + \text{-CH=CH-} \longrightarrow \text{RCOO-CH-CHX} + \text{RCOOAg}$$

A displacement reaction of the type

$$\text{RCOO-CH-CHX} + \text{RCOOAg} \longrightarrow \text{RCOO-CH-CHOOCR} + \text{AgX}$$

might then occur. If the reactions were carried out using a fluorocarbon olefin, the first reaction might conceivably occur. However, the second step would be precluded by the demonstrated fact that hydrogen-free fluorocarbon esters are not obtainable by a reaction of the latter type.

It was shown by Hauptschein and Von Grosse,[15] who attempted to prepare a hydrogen-free fluorocarbon ester by reacting CF_3I with CF_3COOAg in a bomb at elevated temperatures, that ester formation did not occur to any measurable extent. The present writer independently arrived at similar conclusions through the reaction of CF_3COOAg with C_3F_7I in a sealed tube at temperatures up to 250°.

Substitution of Pyridine for X in the Complex-Forming Reaction

Discussion:--In view of the unusual capacity of pyridine for complex formation, it was decided that an experiment involving the substitution of pyridine for X in the reaction of (S) with X would be productive of interesting results -- perhaps leading to the development of a route to alkforylated pyridines by a path of the type

$$\theta COOAg + Py \longrightarrow CO_2 + \theta Py + Ag$$

Pyridine was found to react with (S) at room temperature and in the absence of a solvent in a 1:1 mole ratio. A solid addendum compound, which was isolated and identified, resulted. The preparation and identification of these substances and their subsequent reactions are described in the experimental part of this section.

Experimental -- A. Preparation, purification, and identification.--The substances of the formula $\theta COOPyAg$ were prepared from the silver salts of acetforic acid through valerforic acid. Equimolar quantities of pyridine and (S) are combined under anhydrous conditions at room temperature. Power stirring is employed to mix the reactants thoroughly. An exothermic reaction occurs, which warms the reaction mixture to 45-60°, depending upon the amount of material involved. After the heat of reaction has dissipated, white needle or rhombic crystals are formed. These crystals have the above formula and may be used without further purification in the reactions to be described in the "B" part of this section. However, establishment of formula necessitates removal of any excess pyridine or impurities that may have been present in either reactant.

It was found that (ΘCOO)PyAg is soluble in benzene, chloroform, ether, and boiling heptane or hexane. In the case of ether or chloroform, however, secondary complexing involving the solvent occurs. A second mole of pyridine, if added to this system, results in the precipitation of an unstable, hygroscopic complex, whose formula is approximately (ΘCOO)Py_2Ag. Removal of ether results in gradual decomposition of this material, with the loss of pyridine. An oil results, from which ΘCOOPyAg can be recovered. For example: $C_2F_5COOPyAg$ was dissolved in ether. The solution was chilled to -78° in order to effect recrystallization. No precipitation occurred. A second mole of pyridine was added. White crystals immediately precipitated, thus indicating that C_2F_5COOAg probably can react with 2 moles of pyridine to give a substance of the formula (C_2F_5COO)Py_2Ag. The crystals were separated, and ether was removed in vacuo. A white, highly hygroscopic powder was obtained. The powder had an odor of pyridine and upon analysis was found to contain 26.8 percent silver (theoretical for (C_2F_5COO)Py_2Ag is 25.17 percent). This material, was freed of excess pyridine by washing with anhydrous heptane. The resultant product was found to contain 29.94 percent silver (theoretical for (C_2F_5COO)PyAg is 30.86 percent).

A second experiment of this type, employing a 2:1 mole ratio of pyridine to (S) was conducted. Silver valerforate, 18.5 g. (.05 mole), and pyridine, 7.9 g. (.1 mole), were combined as before. A heavy oil resulted. An attempt was made to remove the excess pyridine by extraction with heptane. This was unsuccessful; the oil

remained undissolved at room temperature. Upon heating, approximately half the oil went into solution. When the solution was cooled to 0°, the oil separated unchanged. The heptane was removed, and the oil dissolved in 100 cc. ether. Upon cooling, crystals were obtained. These were washed with anhydrous heptane and recrystallized from boiling heptane, followed by drying in vacuo. The product, a rather yellow powder, was found to contain 23.49 percent silver (theoretical for $(C_4F_9COO)PyAg$ is 24 percent).

The pure addends were prepared by combining (S) with pyridine in a 1:1 mole ratio and recrystallizing the product from boiling heptane. This solvent was found to be most suitable for the purpose, although the solubility of (ωCOO)PyAg in this medium is rather low even at the boiling point. The solubility was found to increase with chain length. Resistance of (ωCOO)PyAg to hydrolytic action by atmospheric moisture was found to increase with chain length. The analyses were found to approach more nearly the theoretical value as chain length increased.

Data pertaining to the preparation and analysis of the pure addends appear in Table 8.

TABLE 8

PREPARATION AND ANALYSIS OF PYRIDINE ADDENDS OF THE SILVER FLUOROCARBON CARBOXYLATES

(S)	g.	mole	pyridine	mole	Product	% Ag Found	% Ag Theor.
CF_3COOAg	10.0	.045	3.5	.045	$(CF_3COO)PyAg$	35.64	36.00
C_2F_5COOAg	2.0	.007	.57	.007	$(C_2F_5COO)PyAg$	30.31	30.86
C_3F_7COOAg	37.1	.11	6.8	.086	$(C_3F_7COO)PyAg$	26.64	27.00
C_4F_9COOAg	37.1	.10	7.9	.10	$(C_4F_9COO)PyAg$	23.75	24.00

B. Reactions.--If the addends are heated, decarboxylation begins to occur at 160°. Carbon dioxide and fluorocarbon hydride are evolved. Free silver and pyridine are formed, along with a complex mixture of compounds containing fluorine. Pyridinium hydrofluoride and a high-boiling oil, tentatively identified as a difluorobypyridyl, were isolated from this mixture.

When the addend resulting from the addition of pyridine to C_2F_5COOAg was decarboxylated, the above products were identified as follows: Ethforyl hydride was obtained in the cold trap on the exit line from the reactor. It had a molecular weight of 119 (calc. 120). Its infrared spectrum contained the characteristic C-F and C-H absorption bands. If water was excluded from the reaction, C_2F_5H was present in approximately half the total amount available from decarboxylation of (S). If, however, the reactants are not thoroughly dry, a quantity approaching the theoretical value is obtained.

Pyridinium hydrofluoride, obtained in the distillate of the reactor residue, was purified by recrystallization from ethyl alcohol. It was observed to liberate fluoride ion upon solution in water. Treatment with dilute alkali liberated pyridine. Pyridinium hydrofluoride was prepared by reacting pyridine with hydrofluoric acid and recrystallizing the dried product from anhydrous ethanol. Both materials melted 158-162°. However, a mixed melting point was depressed to 148-158°.

An oil boiling 300-304° containing both fluorine and nitrogen was isolated. This material, when dissolved in anhydrous ether and

treated with hydrogen chloride, immediately gave a white precipitate. After repeated washings with ether followed by vacuum drying, the precipitate was analyzed for chlorine and titrated for HCl content.

Two samples analyzed 27.14 and 27.25 percent chlorine. (Calculated values for monofluorobypyridyl dihydrochloride and difluorobypyridyl dihydrochloride are 28.51 and 26.79 percent, respectively.) One sample analyzed 27.93 percent HCl. (Calculated values for the above compounds are 29.3 and 27.54 percent, respectively.) The hydrochloride was found to contain fluorine. These analytical data indicate that the material was a difluorobypyridyl.

The solid residue remaining in the reactor was thoroughly washed free of organic material with ether and heptane, dried, and analyzed for silver. The silver content was found to be 98.9 percent.

Substantially similar results were obtained from the decarboxylation of the complex resulting from the addition of pyridine to silver acetforate. If pyridine and (S) are present in a 1:1 mole ratio, decarboxylation does not occur until a temperature of 220-240° is reached, and considerably more charring and formation of pyridinium hydrofluoride occurs.

Since it was suspected that alkforylation of the pyridine nucleus had occurred to a small extent, it was decided to introduce into the reaction mixture an aromatic substance which would be expected to undergo alkforylation much more readily than pyridine. Experiments were conducted using 2-butyl benzene and meta di-isopropyl benzene. No alkforylation products were isolated.

Results of the above measurements.--Pyridine reacts with (S) in a 1:1 mole ratio to give a crystalline solid, whose analysis indicates it to contain 1 mole of pyridine and 1 mole (S). This substance will decarboxylate at 160-170°, yielding the corresponding fluorocarbon hydride in high yield, along with pyridinium hydrofluoride, mono- and/or di-fluorobypyridyl, and a complex mixture of oils containing fluorine.

This reaction should be investigated more thoroughly, as it shows promise of providing a route to alkforylated pyridines or aromatics.

An Improved Method for the Synthesis of Fluorocarbon Mono-Iodides[8]

Discussion.--A method of preparing fluorocarbon iodides which consisted of the decarboxylation of the silver salt of a fluorocarbon carboxylic acid (S) in the presence of iodine was developed by Simons and Brice.[38] The reaction mixture was kept in suspension in a fluorocarbon diluent by means of mechanical stirring. The process was carried out under strictly anhydrous conditions.

Others[10,14,16] prepared the iodides by heating intimate mixtures of (S) and iodine.

The method herein reported consists of bringing the iodine vapors in contact with (S) under controlled conditions of temperature and pressure without a solid or liquid diluent being present. A sharp reaction zone progresses through the material until (S) is consumed. The fluorocarbon iodide passes from the reactor and is collected as in the original method. Power stirring, and prepurification and drying of the iodine, as well as the limitations imposed by the diluent, are eliminated. Maintenance of anhydrous conditions, recovery of silver and control of reaction temperature are facilitated. Higher product yields are obtained.

Two types of reactors are currently in use in these laboratories, each having advantages depending upon the particular situation. Procedures using these reactors are:

PROCEDURE 1: This method employs a reactor which is simple to construct and provides a quick method of obtaining small quantities

of fluorocarbon iodides in the laboratory. It is also adapted to reactions of this type in which the absence of any atmosphere other than the reaction gases is desired. The reactor is a vertical Pyrex tube, closed at the bottom and stoppered at the top. An exit line attached near the top connects it through two cold traps to a vacuum source. A manometer is attached to the exit line. A KOH tube for removal of CO_2 is placed between the traps and the vacuum source. Reaction temperature is followed by means of a thermocouple or thermometer extending into the tube through the top.

Experimental.--The entire apparatus is vacuum dried. Iodine followed by phosphorus pentoxide (P) is poured into the tube. (S) may be either suspended over the iodine and (P) in a steel-wire cage or poured directly into the tube with a layer of glass wool separating (S) from (P). The apparatus is flushed with dry air. The reactor tube is heated in an oil-bath. The pressure is reduced in order to provide adequate volatilization of iodine at the optimum reaction temperature (130-160°). Completion of reaction is noted by cessation of evolution of gases. The bath is heated to 185° to assure complete conversion of (S). The iodide is collected in the cold traps. All products were fractionated. Iodine was determined by peroxide decomposition and thiosulfate titration. Reaction conditions and yields are in Table 9A.

PROCEDURE 2: This method is superior in cases in which relatively large amounts of various fluorocarbon iodides must be synthesized in the laboratory. The apparatus is shown in Figure 2.

Operation is at atmospheric pressure. A stream of dry air carries the iodine vapor from the pot to the reaction zone. (S) is supported in the reactor by means of a glass "X" member and a thin layer of glass wool. The reactor and the iodine container are separate units whose temperatures are controlled independently.

Experimental.--The apparatus is assembled. (S) is poured into the reactor from the top. Final drying is effected by passing a current of dry air through the reactor while heating it to 70-80°. Excess iodine followed by (P) is placed in the pot. The iodine is heated to sublimation temperature and an extremely gentle air current started. The heat of reaction tends to increase the reactor temperature. The jacket heating is adjusted so as to maintain an optimum reaction temperature of 130-160°. The reaction requires 20-40 minutes, depending on the type and amount of (S). The iodide is collected in cold traps. Purification and identification were carried out as in procedure 1. Reaction conditions and yields are in Table 9B.

Procedure 2 was used in the preparation of C_3F_7Br. No air current was employed. Reflux action of bromine was provided by an ice-water-cooled condenser on the upper end of the reactor. Reaction temperature was 130-150°. Products were fractionated and analyzed for bromine. A 67 percent yield was obtained.

TABLE 9

IMPROVED SYNTHESIS FOR FLUOROCARBON IODIDES

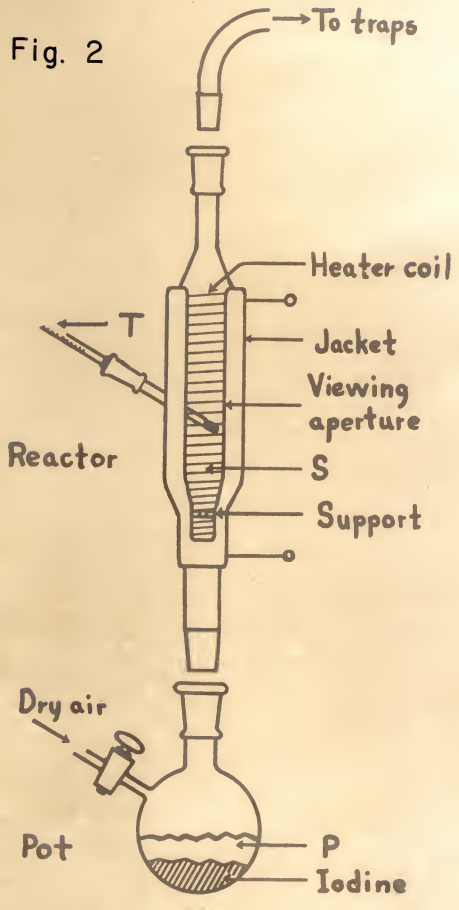
A. Procedure 1

Starting Material	g.	Heating Time, Min.	Operating Temp., °C	Operating Pressure, mm.	Basket Support	Yield, g.	Yield, %
CF_3COOAg	75.1	60	140-150	400-500	Not used	47.6	71
C_3F_7COOAg	15.5	80	140-145	450-500	Not used	13.1	93
CF_3COOAg	75.4	140	150-160	400-500	Used	52.5	78
C_3F_7COOAg	21.2	115	150-160	400-500	Used	16.5	87

B. Procedure 2

Starting Material	g.	Heating Time, Min.	Temp., °C	Yield, g.	Yield, %
CF_3COOAg	33.8	21	150-160	22.3	74
CF_3COOAg	202.1	48	150-160	161.0	90
C_3F_7COOAg	42.0	25	130-160	36.5	94
C_3F_7COOAg	200.4	45	150-160	175.5	95

Fig. 2


To traps
Heater coil
T
Jacket
Viewing aperture
Reactor
S
Support
Dry air
Pot
P
Iodine

Reaction of (S) and the Complex with Phosphorus

Discussion.--Bennet, Brandt, Emeleus, and Haszeldine[2] have described the formation of trimethforyl phosphine and iodomethforyl phosphines from the reaction of phosphorus with methforyl iodide in a closed vessel.

It was decided that the decarboxylation of (S) in the presence of red phosphorus might provide a source of trialkforyl phosphines without resorting to the preparation of the iodide and without obtaining the iodoalkforyl phosphines as by-products.

Instead, the reaction yielded the fluorocarbon carboxylic acid anhydride. The red phosphorus was converted to the yellow allotropic form.

Haszeldine and Sharpe[13] have since reported that a mixture of red phosphorus and silver acetforate yielded acetforic anhydride upon thermal decomposition. The results independently obtained in these laboratories are nevertheless reported here, in some detail, as confirmation and clarification of the work of the above investigators.

The reaction of red phosphorus with the solid complex formed from the reaction of silver acetforate with iodine in the absence of any solvent is described.

Experimental.--Silver acetforate, 75 g. (.34 mole), was mixed with red phosphorus, 26 g. (.84 mole). The mixture was placed in a flask to which was attached a gas collection train. An attempt was made to initiate a self-propagating reaction by heating a small spot on the flask with a gas torch. CO_2 evolution immediately occurred

but stopped as soon as the flame was removed.

The entire flask was then heated with a heating mantle. Decarboxylation began at approximately 200°. Heating was continued until CO_2 evolution ceased. The product was fractionated. The fraction boiling 38.5-40° consisted of 32.5 g. of material. A .5001 g. sample was treated with water. The material reacted violently, liberating acetforic acid which was neutralized by titration of 37.64 cc. of .1266 N. NaOH (correct for acetforic anhydride).

The reactor residue consisted of silver oxide and yellow phosphorus.

Silver acetforate, 45.4 g. (.2054 mole), was mixed with iodine, 25 g. (.0984 mole), in the absence of a solvent. A homogeneous yellow powder resulted, having the composition $CF_3COOAgI$. To this was added a slight excess of red phosphorus. Upon stirring, a homogeneous gray powder was formed. This material spontaneously, and without warning, exploded -- doing considerable damage to both the apparatus and the dignity of the present writer. No products were obtained.

Results of the above measurements.--Silver acetforate (and presumably the higher salts) when decarboxylated with red phosphorus in the absence of any solvent, gives almost a 100 percent yield of acetforic anhydride. The red phosphorus is converted to the yellow form in the process. The equation for the overall process may be written

$$2\ CF_3COOAg + (X)\ P\ (red) \longrightarrow (CF_3CO)_2O + Ag_2O + (X)\ P\ (yellow)$$

The complex mixture of the formula $CF_3COOAgI$ reacts spontaneously with red phosphorus.

RELATED SYNTHETIC PROCEDURES

Preparation of Fluorocarbon Nitriles from (S) and Cyanogen

Discussion.--A novel method for the preparation of fluorocarbon carboxylic acid nitriles which apparently is analogous to previously described fluorocarbon halide syntheses was developed. The method involves the decarboxylation of the silver salt of the fluorocarbon carboxylic acid while passing cyanogen gas through or over the reacting mass. In this procedure, use is made of the halogenoid properties of cyanogen. The overall equation for the reaction may be written

$$\text{RCOOAg} + \text{NCCN} \longrightarrow \text{RCN} + \text{AgCN} + \text{CO}_2$$

Inasmuch as the process was conducted at high temperature and no intermediates were isolated, the author will not hazard the postulation of any mechanism or the suggestion of an initially-formed reaction product involving (S) and cyanogen.

The fluorocarbon carboxylic acid anhydride was isolated from the reaction product along with a small amount of straight-chain fluorocarbon which proved to be the dimer of the fluorocarbon radical involved. The equations for these reactions in which decarboxylation occurs without the involvement of cyanogen may be written

$$2\ \text{RCOOAg} \longrightarrow (\text{RCO})_2\text{O} + \text{Ag}_2\text{O}$$

and

$$2\ \text{RCOOAg} \longrightarrow \text{RR} + 2\ \text{CO}_2 + 2\ \text{Ag}$$

respectively. The decarboxylation of (S) in the absence of other reactive materials has been investigated by Kirshenbaum, Streng, and Hauptschein.[21] Similar products were obtained.

Experimental.--The procedure used in the preparation of butyrforo nitrile is described as follows: The reaction was carried out in a Pyrex tube heated by a muffle furnace. Silver butyrforate mixed with glass chips was packed into the tube. The temperature was slowly raised while maintaining an atmosphere of cyanogen in the tube. The reaction began at approximately 300°. Carbon dioxide was detected by means of a calcium hydroxide scrubber on the exit line. The cyanogen was allowed to stream in at one end while the effluent gases were collected in cold traps connected to the opposite end. The reaction evidently is greatly hindered by the difficulty of providing adequate silver salt-cyanogen contact during the reaction process. The low yields are attributable to this factor, along with the above-mentioned side reactions.

The products were fractionated and identified by physical and chemical properties. A 4.1 g. fraction of clear, inert liquid was obtained, boiling at 55-57° and having a molecular weight of 335 as determined by the Dumas method. (Calc. for C_6F_{14} is 338.) A 6 g. fraction was obtained, boiling at 103-106°. This material reacted violently with water, liberating butyrforic acid. The latter was converted to the amide, which melted at 103-105° (correct for butforamide). Essentially the same procedure was followed in the preparation of valerforo and caproforo nitriles. In every case the nitriles were

hydrolized to the acid by treatment with H_2SO_4 and converted to the methyl ester, from which the amides were prepared. For comparison purposes, the same nitriles were prepared by the conventional method involving dehydration of the acid amide.

Two previously unreported nitriles, C_4F_9CN and $C_5F_{11}CN$, were prepared. Nitrogen analyses on these were performed by Peninsular ChemResearch, Inc.

Experimental data appear in Table 10A. Analytical data appear in Table 10B.

Results of the above measurements.--The investigation was undertaken in order to determine if the previously described method for the preparation of fluorocarbon halides by the decarboxylation of (S) in contact with the vapors of X could be extended to the use of compounds described as "pseudo halogens" or "halogenoids" in place of X. The reaction reported, though hardly a practical means of preparing fluorocarbon carboxylic acid nitriles, serves to illustrate the "halogenoid" character of cyanogen as related to reactions of this type.

TABLE 10

PREPARATION OF FLUOROCARBON NITRILES BY THE DECARBOXYLATION OF SILVER SALTS OF FLUOROCARBON CARBOXYLIC ACIDS IN THE PRESENCE OF CYANOGEN

A. Experimental Data

(S)	g.	moles	Reactor Temp., °C	Nitrile Obtained	g.	moles	Yield, %
C_3F_7COOAg	40	.125	340-350	C_3F_7CN	5.6	.029	23
C_4F_9COOAg	88	.237	350	C_4F_9CN	7.5	.031	13.1
$C_5F_{11}COOAg$	85	.203	350	$C_5F_{11}CN$	6.1	.021	10

B. Analytical Data

Nitrile	Source	B.P.	Mol. Wgt.	Nitrogen, % Calc.	Nitrogen, % Found	Amide M.P.	Mixed M.P.
C_3F_7CN	From (S)	-1 — +1	143			103	
	Literature	-1 — +1	145			105	
C_4F_9CN	From (S)	28.5	196	5.72	5.63	110	110
	From Amide	28.0	196			111	
$C_5F_{11}CN$	From (S)	56.0	244	4.75	4.55	115	114
	From Amide	56.0	245			114	

Synthesis of Fluorocarbon Mono-Iodides
from Fluorocarbon Carboxylic Acid Anhydrides

Discussion.--It was discovered that fluorocarbon mono-iodides can be prepared continuously by passing a vaporized mixture of iodine and fluorocarbon carboxylic acid anhydride through a hot tube containing silver iodide. In this procedure, the anhydride is made as a part of the overall process, thus providing a method for going from the fluorocarbon carboxylic acid to the corresponding iodide in one procedural step. The overall equation for the reaction may be written

$$(\Theta COO)_2O + I_2 \longrightarrow 2\ \Theta I + CO_2 + CO$$

The function of the silver iodide is not clear. However, its beneficial effect is evident upon comparison of the results obtained with and without this material in the reactor tube.

Haszeldine[12] prepared methforyl iodide by heating acetforic anhydride with iodine at 350° for 12 hours, presumably in a sealed vessel.

Experimental.--The fluorocarbon carboxylic acid is metered into a heated three-neck flask containing phosphorus pentoxide. To one neck of the flask is attached a line through which dry air can be admitted, if necessary, to carry the reactant vapors into the reactor tube. The anhydride is formed by reaction of the acid with phosphorus pentoxide, and passes out through the other neck of the flask into a large tube leading into a furnace. A flask containing iodine and phosphorus pentoxide is also connected to this tube. The flask is heated, causing the iodine to sublime into the tube and mix with the vapors of anhydride

passing into the furnace. The silver iodide, mixed with glass chips, is packed into the heated portion of the tube. The mixed vapors pass through and over the silver iodide. A condenser is provided at the exit end of the tube to prevent the passage of iodine into the collecting traps. The product, along with some unreacted anhydride, is collected in the traps which are appropriately cooled, depending upon the boiling points of the products being formed. Evolution of carbon dioxide is detected by means of a calcium hydroxide scrubber attached to the exit line. Reactor temperatures ranging from 300° to 400° were employed, although at the higher temperatures decomposition begins to occur, as evidenced by the appearance of fluoride ion in the calcium hydroxide scrubber. Experimental data and product yields appear in Table 11.

All products were fractionated. Fluorocarbon iodides were identified from fractionation data and molecular weights. The latter were determined by the Dumas method.

Results of the above measurements.--The presence of silver iodide in the reactor tube has a definite beneficial effect, both on conversion and yield. The latter term is based on the amount of unrecoverable acid. Lower reactor temperatures can be employed with resultant decrease in the formation of decomposition products. The overall yields are correspondingly improved. Apparently the optimum reactor temperature is around 325° for the materials investigated. Higher conversions might be achieved through the use of a longer reactor tube with specially prepared and supported silver iodide.

A reactor designed to re-cycle the unreacted anhydride might also achieve the same end. However, time in which to do further development work on this interesting synthetic procedure was not available.

TABLE 11

PREPARATION OF FLUOROCARBON IODIDES FROM FLUOROCARBON CARBOXYLIC ACID ANHYDRIDES

Acid	g.	moles	AgI	Temp. °C	Iodide Obtained, g.	moles	Conversion, %	Anhydride Recovered, g.	Acid Consumed, moles	Yield, %
CF_3COOH	38.42	.337	Not Used	350-700	2	.01	3	---	---	--
CF_3COOH	55.18	.484	Not Used	400-600	10.4	.053	11	20.0	.294	18
C_3F_7COOH	21.53	.1006	Not Used	355-510	1.8	.0061	6	5.16	.0766	8
CF_3COOH	25.54	.224	Used	300-360	7.2	.0367	16.3	8.88	.1394	26
CF_3COOH	51.3	.450	Used	200-330	10.3	.0525	11.7	23.0	.2300	23
C_3F_7COOH	16.14	.0754	Used	230-400	9.0	.0304	40	5.16	.0502	62

DISCUSSION OF RESULTS

The investigation reported in this dissertation was undertaken in order to expand the knowledge pertaining to the fluorocarbon carboxylic acids. Special attention was given to the identification and characterization of the intermediates in the reactions between the silver salts of these acids and halogen or halogen-like materials.

The author feels that this end was achieved insofar as iodine and bromine are concerned. Chlorine and fluorine were not included in this investigation, as their physical and chemical properties render them unadaptable to the experimental procedures developed and used for the reactions involving iodine and bromine. The author wishes to point out that no extrapolation of the findings reported for iodine and bromine to the other halogens is either stated or implied.

It was found that when iodine or bromine are combined with (S) in a completely inert solvent at temperatures below those at which decarboxylation can occur, one equivalent of X is consumed for each equivalent of (S) present. It was further demonstrated that any X added past this point is present only in the free state.

Inert fluorocarbons and fluorocarbon derivatives were found to be the only solvents suited to an investigation of this type. The product of the addition of X to (S) under these conditions was found

to be an addendum compound of the formula $(\Theta COO)_2AgX$. These substances were characterized in solution in OF solvents by determining the relationship between acid content, oxidizing power, and silver content. Addends of the formula $(\Theta COO)_2AgI$ were isolated and identified.

The complexes can be isolated for analysis only by crystallization from solution at reduced temperature. They undergo partial or total decomposition if allowed to warm to room temperature in the absence of a solvent. However, the substance $(\Theta COO)_2AgX$ apparently is stabilized by the presence of another mole of AgX, forming an insoluble material of the empirical formula $\Theta COOAgX$, which is relatively stable in the absence of moisture.

$(\Theta COO)_2AgI$ is stable in solution. $(\Theta COO)_2AgBr$, however, gradually decomposes, as evidenced by decrease in oxidizing power with time. Stability of the complexes was also observed to increase with chain length.

Pyridine was found to undergo a complex formation with (S). The complexes can be isolated and purified by recrystallization from ether, and were found to have the general formula $(\Theta COO)PyAg$. The pyridine complex undergoes decarboxylation at 160° with the formation of the corresponding fluorocarbon hydride, pyridinium hydrofluoride, and a number of other fluorine-containing products. This reaction shows promise of providing a route to alkforylated pyridines or aromatics.

The silver salts of fluorocarbon carboxylic acids can be decarboxylated in the presence of red phosphorus to give the

corresponding anhydride in high yields. The complex mixture $\theta COOAgI$ explodes on treatment with red phosphorus.

An improved synthesis for fluorocarbon iodides was developed which produces higher yields and eliminates many of the tedious and time-consuming operations previously inherent in the procedure.

Fluorocarbon carboxylic acid nitriles can be prepared by decarboxylating (S) in the presence of cyanogen. The reaction apparently analogous to the above iodide preparation in that cyanogen behaves in a halogen-like manner under the reaction conditions.

A process was developed for the preparation of fluorocarbon iodides by a decarboxylation-decarbonylation of a fluorocarbon carboxylic acid anhydride in the presence of iodine. The yields and conversions are improved markedly by the presence of silver iodide in the reactor.

Through the isolation, characterization, and establishment of the formula of the halogen addends of the silver salts of the silver fluorocarbon carboxylates, the author feels that some light has been shed on an area in which considerable confusion and disagreement existed.

By comparison of the data found in this investigation with that available on the reactions of the salts of the hydrocarbon carboxylic acids with the halogens, considerable insight into the fundamental differences existing between the fluorocarbon carboxylic acids and their organic counterparts can be gained.

A number of interesting and useful processes have been

developed in the course of this investigation. Also, several reactions were discovered which may provide avenues for future research.

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VITA

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This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of the committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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